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(54) **Process for producing deep cleaned coal**

(57) Coal of no greater than 600  $\mu\text{m}$  (28 mesh) is immersed in an organic solvent comprising butylamine, propylamine or ethylenediamine for a sufficient time to induce swelling and natural fracture of the coal. The mixture is distilled to recover the solvent and the swelled coal is chemically leached with hydrogen peroxide and selected acids to produce deep cleaned coal fines.

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## SPECIFICATION

## Process for producing deep cleaned coal

- 5 The invention relates to the production of deep cleaned coal by a physio-chemical cleaning. 5

There is a pressing need for an effective and economical method for cleaning coal which would encourage increased use of coal as an alternative utility energy source and meet air-quality standards without the use of flue gas desulphurization systems. Deep cleaned coal, containing less than 1% sulphur and 1% ash, not only can satisfy most current air-quality standards, but 10 also is a potential alternative fuel in oil or gas-fired units. The low ash level, in particular, would allow use of coal with minimal derating of equipment due to slagging, fouling, and erosion of heat transfer surfaces, thereby also improving the performance of coal combustion equipment. 10

Extensive research in deep coal cleaning is ongoing and uses either advanced physical or chemical cleaning approaches. Physical cleaning of coal employs mechanical grinding to liberate 15 mineral impurities followed by selective separation to recover the cleaned product. Highly efficient comminution processes must be employed to obtain the extremely fine grinding needed for liberating mineral matter from the coal. In addition, high performance separation techniques are required for removing the fine ground mineral matter from the coal. The similarity of the surface and chemical characteristics of coal fines and mineral matter, especially pyrite, further compli- 20 cates the separation, particularly as regards separation techniques that depend upon surface property differences for separation. Thus, the efficiency of physical cleaning depends on the degree of mineral liberation and the effectiveness of the selective separation technique. Usually, the more finely the coal is ground, the better the mineral liberation. Although ultrafine grinding (approximate maximum size of 100  $\mu\text{m}$ ) can help achieve maximum ash mineral liberation for 25 most coals, it also can cause difficulties in downstream separation of coal fines without contamination by fine mineral particles and excessive power loss. 20

Existing advanced physical cleaning processes, with sophisticated separation techniques, such as selective oil agglomeration or selective flocculation procedures, can produce deep clean coal products containing less than 3% residual ash mineral content, but they all have to grind the 30 coal down to the sub  $\mu\text{m}$  particle size range before separation. The high energy consumption associated with ultrafine grinding, however, leads to an unacceptably high cost of production of the deep cleaned coal. It has been observed that the energy consumption for grinding coal to a size no greater than 10  $\mu\text{m}$  is as high as  $10.8 \times 10^5$  Joules/kilogram. Moreover, the inability of processes, such as selective oil agglomeration or selective flocculation procedures, to remove 35 organic sulphur from coal limits the applicability of these advanced physical cleaning technologies to deep clean coal production. 30

Some chemical cleaning methods use chemical reagents to convert the solid mineral impurities into soluble or gaseous species which are then separated from the cleaned coal. Processing conditions which must be controlled include chemical concentration, temperature, pressure, and 40 residence time. Difficulties in chemical cleaning of coal include maximizing the level of ash and sulphur reduction while minimizing volatile matter loss, undesirable side reactions, power loss, and operating costs. 40

While some existing advanced chemical cleaning processes can remove a high percentage of ash and a portion of organic sulphur, they also require intensive processing conditions. The TRW 45 Gravimelt process, for example, can remove almost all the ash and up to 70% of the organic sulphur from coal with a molten caustic mixture of alkali metal hydroxide at 390°C for 2 to 4 hours. These conditions, however, may cause volatile matter loss. The Ames Lab Wet Oxidation Process requires pressure and temperature which result in non-selective oxidation reactions, causing heat loss and low efficiency in coal sulphur removal. Also available chlorinolysis pro- 50 cesses involve multiple steps, including a high temperature dechlorination procedure (up to 700°C), which leaves a cleaned char product. 50

According to the invention there is provided a process for producing deep cleaned coal comprising the steps of:  
providing a supply of air-dried coal of particle size fractions of 600  $\mu\text{m}$  (minus 28 mesh) or finer; 55  
immersing the coal in an organic solvent comprising butylamine, propylamine or ethylene diamine to form a mixture, having coal in an amount to provide no greater than 40 weight percent solids content, for a time period sufficient to swell the coal and to induce natural fracturing of the coal; distilling the mixture to recover the organic solvent;  
subjecting the swelled coal to leaching with a 10 to 20% aqueous hydrogen peroxide solution 60 containing 1 to 2% sulphuric acid at ambient conditions; and  
subjecting the swelled coal to leaching with an aqueous solution containing 3 to 6% ammonium hydrogen fluoride and 2 to 3% of nitric acid or hydrochloric acid. 60

The invention results from an innovative approach to producing deep cleaned coal at milder operating conditions and with lower energy consumption by employing coal swelling technology 65 to swell the coal, causing it to become more porous. This enhances the liberation of ash 65

impurities and facilitates better mass transport of chemical reagents for reaction with unliberated ash impurities. The swelled porous coal also enhances evolution of the organic sulphur from the matrix during thermal hydrodesulphurization.

Natural fracturing means that the fracturing is not caused by conventional mechanical force but by the solvent weakening the coal intermolecular cross-linkages and by the differences in the swellability of the various subcomponents such as macerals and mineral matter, causing uneven swelling within the coal. Such uneven swelling induces distortion and stresses and finally fractures the coal. The solvents are recovered for recycling by distillation at their boiling point or at lower temperatures under partial vacuum. The swelled coal can either be directly subjected to chemical leaching steps or subjected to a physical separation process before application of chemical leaching procedures.

Leaching the coal in an aqueous solution containing hydrogen peroxide and sulphuric acid, preferably with continuous agitation at ambient temperature and pressure, removes residual pyrite. After coal has been separated from the solution the step of leaching the coal in an aqueous solution containing ammonium hydrogen fluoride, and hydrochloric acid preferably at a temperature of 50°C to 80°C and at ambient pressure is effected to remove the residual ash. The coal can subsequently be filtered and washed with water until the water shows a neutral pH and then dried and prepared for organic sulphur removal. The dried coal is transferred to a reactor and subjected to a regulated flow rate of hydrogen at about 400°C for a predetermined time. After this treatment, the coal is collected as a deep cleaned product.

In one specific embodiment air-dried coal to be treated in accordance with the process is first subjected to swelling, by soaking the coal in an organic solvent at a 30 to 40 weight percent solids content for a time period sufficient to induce natural fracture to approximately minus 100 mesh particle size. The time for swelling is approximately 6 to 8 hours, depending on the coal and its initial particle size.

The initial particle size of the coal should be no greater than 600  $\mu\text{m}$ . The solvents are recovered for recycling by distillation at their boiling point, or alternatively, by boiling at lower temperatures under partial vacuum.

The solvents swell the coal by weakening the intermolecular cross-linkage and causing natural fracturing along surfaces between the organic matrix and impurities. The swelling causes the coal to become more friable towards grinding and enhances the liberation of ash impurities.

The swelled coal is subjected to grinding to a size range of 600  $\mu\text{m}$  (minus 28 mesh) or finer. At this stage, coal ash mineral impurities are partly liberated and partly still encased inside coal particles. A physical separation, such as float/sink or froth flotation, can be used to remove most of the liberated ash mineral impurities, leaving the residue mineral impurities to be removed chemically. In this way, the physical separation can help to reduce the chemical consumption in the chemical leaching steps. However, the swelled coal could also be subjected directly to chemical leaching without physical separation.

Thereafter, chemical leaching is used to remove residue impurity fines. The fine pyrite is removed by leaching with a 10 to 20%, preferably 20%, aqueous hydrogen peroxide solution containing 1 to 2% sulphuric acid at ambient conditions. Other mineral matter, mostly aluminum silicate, is removed by leaching with an aqueous solution containing 3 to 6%, preferably 6%, of ammonium hydrogen fluoride and 2 to 3% of nitric acid at a moderate temperature such as 70°C and ambient pressure. The time needed for leaching is about one to two hours depending on the coal and its particle size.

Organic sulphur in coal has been shown to contain aliphatic and aromatic sulfides, disulfides, thios, and thiophenes. The thiosulfide and disulfide sulphur, which is about 30 to 50% of total organic sulphur, is removed easily by hydrodesulphurization for short periods, 10 to 20 minutes for 600  $\mu\text{m}$  (minus 28 mesh) size coal, at temperatures around 400°C, preferably not above 400°C, without losing significant volatile matter. The volatile matter release profile indicates a low rate of release for most coals at these temperatures.

The following examples and tables are illustrative and explanatory of the invention. All percentages are expressed as weight percentages unless otherwise indicated.

#### 55 EXAMPLE 1

Forty grams of 6mm to 1.7mm (1/4 inch  $\times$  10 mesh) Kentucky No. 9 coal were air-dried and transferred into a 500 ml round bottom flask. Then, 120 ml of ethylene diamine was added to the coal and the mixture was allowed to sit for eight hours with occasional stirring. The solvent was then recovered by evaporation at a temperature of 78°C under partial vacuum, using a nitrogen gas purge. The solvent was collected by condensation in a flask immersed in an ice bath. The solvent recovered was 95 percent by weight of the amount added and transparent in appearance. The swelled coal appeared dry and more friable as indicated by the ease with which it could be crushed with finger pressure. The swelled coal was then crushed to 150  $\mu\text{m}$  (minus 100 mesh) particle size and added to an 800ml beaker containing 500ml of standardized gravity heavy liquid medium, such as certigrav liquid, having a specific gravity of 1.6. The float portion

(coal) at 1.6 specific gravity was collected and dried in air to prepare it for the chemical cleaning process. The dried coal was added to a 500ml beaker containing 100ml of 20% hydrogen peroxide and 1.5ml of concentrated sulphuric acid and 98.5ml of water. The mixture was stirred for about one hour at ambient temperature and pressure before filtration and water washing. The resulting coal was then added to a 500ml beaker containing 15 grams of ammonium hydrogen fluoride, 40ml of concentrated hydrochloric acid and 220ml of water. The mixture was heated to 70°C for an hour and was separated by filtration and water washed. This product was then dried in air and placed into a vertical reactor where it was purged with nitrogen. It was then heated to 390°C under a nitrogen and hydrogen gas mixture (1 to 3 ratio at 250 ml/minute) for 20 minutes. The hydro-desulphurized coal was then cooled under nitrogen and finally collected for chemical analysis. The results are shown in Table 1.

#### EXAMPLE II

Forty grams of prewashed Ohio No. 6, containing 6.8% by weight ash, was treated exactly as in Example I, except that the float/sink separation step was omitted because of the low initial ash content in the raw coal. The results are shown in Table 2.

TABLE I

20	<u>Kentucky No. 9</u>	<u>Raw Coal</u>	<u>Swelled Coal 1.6 Float</u>	<u>Treated Coal</u>	20
25	Weight, gm	40	36.5	31.2	25
	Particle Size	6mm to 1.7mm ( $\frac{1}{4}$ inch x 10 mesh)	150 $\mu$ m (-100 mesh)	150 $\mu$ m (-100 mesh)	
	Ash, %	12.2	6.7	1.2	
30	Total Sulphur, %	4.72	-	1.3	30
	Pyritic, %	1.84	-	0.3	
	Organic Sulphur, %	2.72	-	1.0	
35	Volatile Matter, %	39.8	-	35.5	35
	Nitrogen, %	1.47	-	1.63	
40					40

TABLE II

45	<u>Ohio No. 6</u>	<u>Raw Coal</u>	<u>Treated Coal</u>	45
	Weight, gm	40	36	
50	Particle Size	6mm to 1.7mm ( $\frac{1}{4}$ inch x 10 mesh)	150 $\mu$ m (-100 mesh)	50
	Ash, %	6.82	1.05	
55	Total Sulphur, %	2.28	1.40	55
	Pyritic, %	0.7	0.3	
	Organic Sulphur, %	1.42	1.0	
60	Volatile Matter, %	41.7	40.5	60
	Nitrogen, %	1.5	1.3	

The results of the tests in the two examples indicate that the process achieved removal of up to 91% ash, 72% total sulphur and 46% organic sulphur from the raw coal, in Example I, without

large losses in volatile matter content. A similar result is demonstrated by the results of Example II.

- Use of the process for coal beneficiation provides several advantages over the existing advanced physical and advanced chemical cleaning processes. Application of swell technology to induce a natural fracturing in the coal, makes it more friable and promotes the efficient liberation of mineral matter in its inherent particle size. this helps to minimize the production of mineral fines, which accompanies ultrafine grinding normally required to maximise mineral liberation. Minerals are removed after swelling by relatively mild crushing. Since the swelled coal is more porous, mass transport of the chemical reagents is enhanced in downstream chemical treatment for removing residual mineral impurities and organic sulphur by hydrosulphurization. This allows milder treatment conditions as regards temperature, pressure, residence time, and reagent concentration for removal of finely disseminated mineral impurities. The evidence of the swelled coal facilitating better mass transport was observed by comparing the swell rate of a raw coal to that of swelled coal in the same solvent under the same conditions. In a test of Ohio Sunnyhill seam coal 6mm x 1.7mm (1/4 x 10 mesh) with n-butylamine, it took 6 hours for the raw coal to attain the maximum swell, but it took less than one hour for a dried swelled coal to be swelled again to attain the same maximum volume. This means that it is much easier for the solvent to penetrate into a swelled coal than into the raw coal.
- The process is physiochemical in that it takes advantage of both physical and chemical cleaning processes. More coarse mineral particles are removed during physical separation and finely disseminated mineral particles are dissolved by milder chemical leaching. Thus, the process avoids energy intensive ultrafine grinding and difficult separation of mineral fines typical of most advanced physical cleaning processes. The process can avoid the vigorous operating conditions which are often cited as major obstacles for application of chemical treatment of coal cleaning. Furthermore, the hydrogendesulphurization of swelled coal under relatively mild conditions can achieve favourable organic sulphur reductions compared with other existing chemical processes, without loss of significant volatile matter.

#### CLAIMS

1. A process for producing deep cleaned coal comprising the steps of: providing a supply of air-dried coal of particle size fractions of 600  $\mu\text{m}$  (minus 28 mesh) or finer; immersing the coal in an organic solvent comprising butylamine, propylamine or ethylene diamine to form a mixture, having coal in an amount to provide no greater than 40 weight percent solids content, for a time period sufficient to swell the coal and to induce natural fracturing of the coal; distilling the mixture to recover the organic solvent; subjecting the swelled coal to leaching with a 10 to 20% aqueous hydrogen peroxide solution containing 1 to 2% sulphuric acid at ambient conditions; and subjecting the swelled coal to leaching with an aqueous solution containing 3 to 6% ammonium hydrogen fluoride and 2 to 3% of nitric acid or hydrochloric acid.
2. A process for producing deep cleaned coal according to claim 1, including the step of heating the swelled and leached coal to about 390°C under a nitrogen and hydrogen gas mixture for a time sufficient to form hydrodesulphurized coal.
3. A process for producing deep cleaned coal substantially as hereinbefore described in Example I or Example II.